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WIDTHS OF HCl OVERTONE LINES AT VARIOUS TEMPERATURES*

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ABSTRACT

In an effort to elucidate the roles of the various factors contributing to the self-broadening of molecular lines, width measurements have been made on the overtone band of HCl at several temperatures from 200° K (dry ice) up to 1283° K. The first 10 lines of the *R*-branch were chosen for study and the recorded data were subjected to treatment by the equivalent width method and by direct analysis of the transmission curve widths, peaks, and slopes.

The general pressure broadening theory of Anderson as amplified by Tsao and Curnutte is readily adaptable to the conditions of the present investigation. Calculations based thereon and incorporating the resonant dipole interaction in combination with a non-resonant term which maintains a ("billiard ball") lower limit to the collision cross section at an intermolecular distance, r_0, yield widths which generally agree well with the experimental data. The values of the billiard ball cross section ultimately chosen to give an adequate fit were r_0 = 6.2, 6.0, 5.7, and 5.5 A corresponding to the temperatures 200, 300, 513, and 1283° K.

INTRODUCTION

The work reported here encompasses an investigation of the widths of individual HCl overtone lines, self-broadened, over a rather wide range of temperature, together with an analysis of methods appropriate thereto.

The first measurements of the widths of individual infrared absorption lines were undertaken in the photographic infrared and are represented by the investigations of Herzberg and Spinks (1934), Lindholm (1942), and Kortum and Verleger (1950). Self-broadened widths of individual HCl lines have been measured in the fundamental by Benedict, Herman, Moore, and Silverman (1956) and by Babrov, Ameer, and Benesch (1959), and in the overtone by Jaffe, Kimel, and Hirshfeld (1962). The temperature dependence of individual line widths has been investigated by Smith, Lackner, and Volkov (1957), who worked in the microwave region, and by Smith (1961), who measured the lines of the HF fundamental. Finally, Benedict, Herman, Moore, Silverman (1961) have reported measurements made on the HCl fundamental at several temperatures.

EXPERIMENTAL

The spectra which constitute the basis for the present investigation were obtained using the spectrometer portion of the Rehovot spectrometer–refractometer, which has been described previously (Jaffe 1961). The light source

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was a 100-watt Zr arc lamp, the radiation from which was chopped immediately after emergence and focussed to the center of one of a family of interchangeable quartz absorption cells mounted in an oven. An alternative arrangement passed the light through a cell composed of three serial sections, the central section (containing the HCl) being cooled with dry ice and the outer sections being evacuated to eliminate fogging.

The furnace used for heating the absorption cell had the form of a large hollow box, on the inner walls of which were mounted the heating elements. The absorption cell was introduced through a circular opening in the furnace end wall and permitted to rest lightly on a piece of fired clay. It was supported further by a small quartz tube through which it remained connected to the gas handling system for continuous monitoring of the pressure. In this position, the cell was well removed from all of the furnace walls so that the effect of local thermal gradients was minimized. As a precaution against temperature variations due to incoming air currents, the furnace orifices were covered with quartz windows. The temperature in the oven could be raised to 1000° C, at which point it could be held constant to within ±5° C.

Figure 1 shows a fast scan of the hot HCl overtone spectrum.

The spectra of the individual lines were recorded using a screw-driven thin wedge type scanner (Rank *et al.* 1953; Shearer and Wiggins 1955). Care was taken to extend the records beyond the farthest discernible wings of the lines in order to establish the zero-absorption signal which was corrected for the effect of scattered light (about 1%).

A preliminary measurement which had to be made was the determination of the slit function and its width. This measurement was carried out with the Hg^{198} 1.3673 μ line, and a slit function which could be closely approximated by a triangle was obtained. The width of the slit function is half the width of the base of this triangle. When measured on the recording paper, this number is independent of wavelength for a constant speed of recording paper.

DATA PROCESSING

The measurement of the line widths was based on two principal methods which served to complement one another. One was the equivalent width method. This scheme has already been described in great detail by many authors, for example, Benedict *et al.* (1956) and Babrov *et al.* (1959). Assuming that the line strengths are known, the widths of lines in or near the so-called square root region may be calculated from their measured equivalent widths.

One of the limitations on the equivalent width method of measuring line widths and strengths arises from the ultimate intrusion of the transmission curve of an absorption line upon that of one of its neighbors as the equivalent width is, from whatever cause, increased. This general problem of the analysis of overlapping lines has received considerable attention in the past, since it bears heavily on the problem of atmospheric transmission of radiation. Furthermore, Benedict *et al.* (1956) have made a brief but systematic check of the region of breakdown of the reliability of the equivalent width method and have presented the results in a form which is most cogent to the present

PLATE I

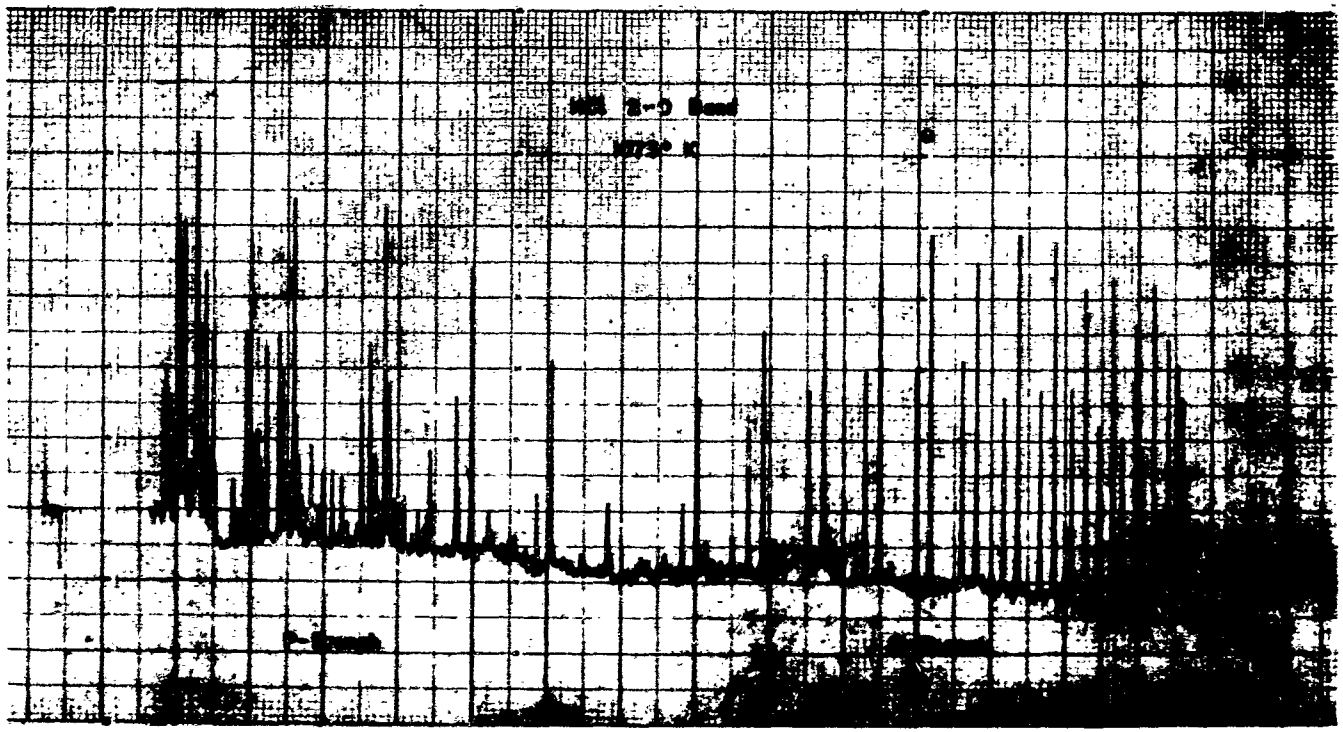

FIG. 1. Absorption spectrum of HCl in the 2-0 band. At the right end of the *R*-branch the band head can be seen. The *P*-branch is partly obscured by water vapor.

investigation. On a practical level, however, the issue need not be approached with particular caution in a study of individual lines, since the approximate extent of the overlap is usually obvious from the record, and the gravity of the corresponding distortion of the equivalent width may therefore be estimated.

In the case of the spectra taken at room temperature with a 50-cm absorption cell, the extraction of meaningful equivalent widths for either of the isotopic components was considered quite impractical for lines $R(0)$ to, say, $R(6)$. At pressures of more than a few centimeters of mercury, these lines begin to overlap, and measurements of the widths were made using the following method.

SLICING

Consider the reproduction of the chart of the $R(1)$ isotopic pair as given in Fig. 2. The areas of such lines are ill-defined, as indicated above, and the half width is inaccessible to direct measurement due to the strong saturation. As pointed out by Benedict *et al.* (1956), however, a creditable measurement of the breadth of the transmission curve (not necessarily at half the maximum transmission) can easily be made. Furthermore, for such a measurement the accuracy of the data will depend not on the ratio of slit width to line width but on the ratio of slit width to transmission curve breadth. Thus a heavily saturated line is favored for these direct measurements on the transmission curve. This point will be dealt with in some detail in the section on corrections.

Typically, five or six measurements of the transmission curve breadth would be made at convenient levels marked on the recorder chart. These "slices" are shown as the heavy horizontal lines in Fig. 2 and measurements appropriate to the third slice are indicated. Thus, the data to be collected for the third slice include the transmission curve breadth, b_ϵ, at that level, the signal intensity, I_3, at that level, and the signal intensity in the absence of absorption, I_0. With these values in hand, one reasons as follows.

In the absence of instrumental distortion, the transmission at each point on the curve is given by $T = e^{-\epsilon}$, where

$$\epsilon = \frac{SL}{\pi} \frac{\gamma}{(\nu-\nu_0)^2+\gamma^2}, \tag{1}$$

the Lorentz line. S is the line strength, L is the cell length, and γ is the line width.

Then, inserting for $(\nu-\nu_0)$ its measured value of $b_\epsilon/2$ and solving for γ, we obtain

$$\gamma_\pm = \frac{SL}{2\pi\epsilon}\left[1 \pm \sqrt{\left(1-\frac{b_\epsilon^2\epsilon^2\pi^2}{S^2L^2}\right)}\right]. \tag{2}$$

To extract a γ from the level 3 data, one inserts into the relation above the negative logarithm of the transmission at that level, ϵ, as well as b_ϵ, the line strength, and the cell length. In the example at hand, six values of γ are obtained from the six slices shown. In general, those values taken from near the top of the line are most subject to instrumental distortion, since it is there that the curvature of the true transmission curve changes most rapidly.

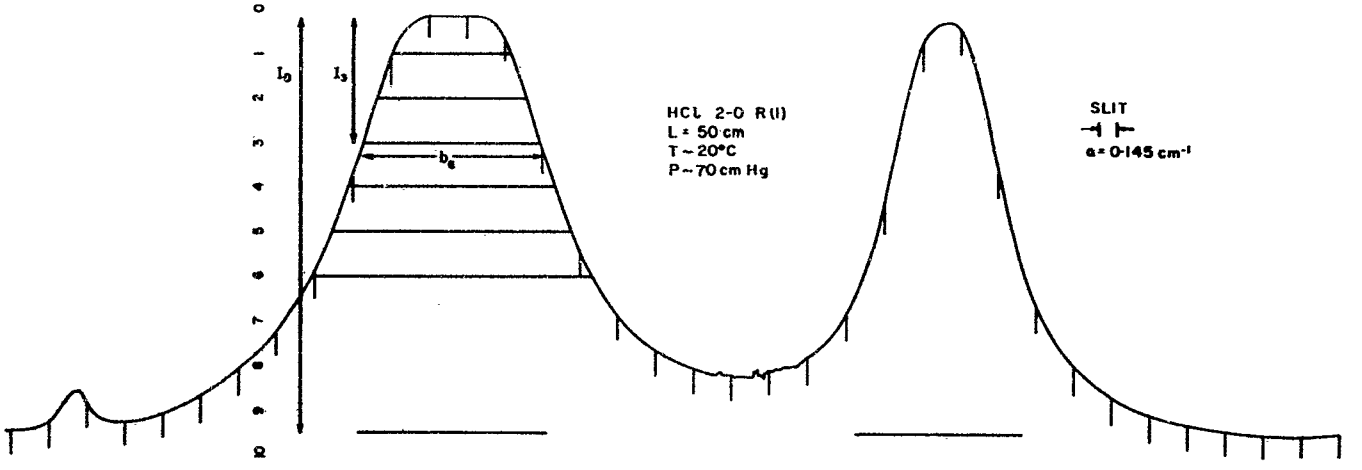

FIG. 2. This reproduction of an isotopic pair of HCl overtone lines illustrates the application of the slicing method of obtaining line widths. The small line at the left is due to absorption by water vapor.

The values taken from near the bottom of the line are jeopardized by the increasing sensitivity of the computed γ to the accuracy of the measured transmission, since for values of transmission near unity any fluctuation produces a severe percentage change in the logarithm. Furthermore, for measurements distant from the line center, the influence of the isotopic component of the line looms as a threat to the accuracy of the data.

In spite of these dangers, a set of five or six slices of a strong line will typically yield three or four values of γ from adjacent slices which are in reasonably good agreement. Data taken from the example of $R(1)$ in Fig. 2 gave the following ϵ's and γ's:

Level	ϵ	γ, cm^{-1}
1	2.38	0.206
2	1.62	0.210
3	1.19	0.207
4	0.88	0.205
5	0.66	0.203
6	0.47	0.196

Here the first five values agree quite well while level 6 gives a slightly lower γ, presumably because of the uncertainty in the decreasing extinction coefficient, ϵ.

In solving for γ (eq. 2) in the above example, the negative radical was chosen and indeed such a choice is justified for all cases of heavily saturated lines. As illustrated in Fig. 3, which is typical of the data for room temperature and below, the specification of S, L, b_ϵ, and ϵ results in the selection of just two

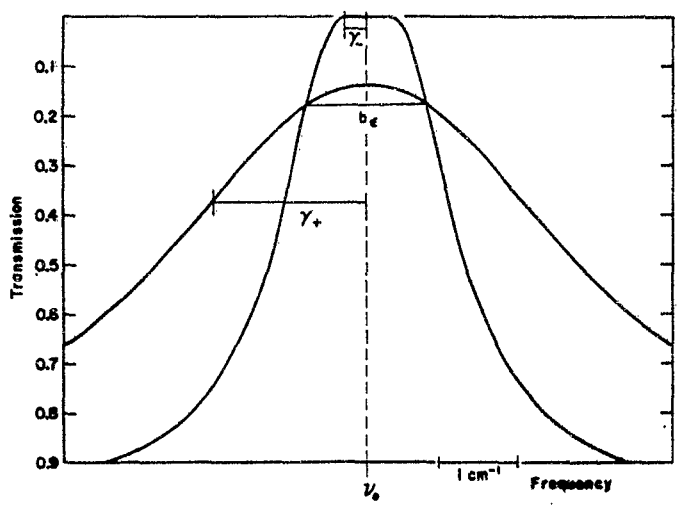

FIG. 3. The ambiguity of the slicing method. To each given set of values of S, b_ϵ, ϵ, L, there correspond two transmission curves, one with half width γ_+, the other with half width γ_-. In practice the two cases are easily distinguished.

possible Lorentz transmission curves passing through the endpoints of the slice b_ϵ. In general, one of the possible curves will have a width, γ_+, greater than b_ϵ and the other a width, γ_-, smaller than b_ϵ, the difference between the two γ's increasing as the slice level increasingly differs from the level corresponding to the half height of the extinction coefficient curve.

As a limiting case, should the slice be taken at the half-width level, then $b_\epsilon = 2\gamma$. Turning to eq. 1, it is seen that at that level the extinction coefficient may be written

$$\frac{\epsilon_0}{2} = \frac{SL}{2\pi\gamma} = \epsilon_{1/2}$$

whence

$$(\epsilon_{1/2})^2 = \frac{S^2L^2}{4\pi^2\gamma^2}$$

and inserting this value into the radical there results

$$\gamma = \frac{SL}{2\pi\epsilon_{1/2}}[1 \pm \sqrt{(1 - b_\epsilon^2/4\gamma^2)}].$$

Thus the radical vanishes and there is but one curve consistent with the four specified values of S, L, b_ϵ, and ϵ.

The foregoing exposition of the slicing procedure and its attributes has dealt with the transmission curve as a directly observable function or as it would be recorded by a spectrometer of infinite resolution. At the two lowest temperatures with which this work is concerned, the instrumental smearing is not sufficiently serious to introduce appreciable error into the data obtained by slicing the first five lines of the R branch. At higher values of m and for the 240° C data, however, it was found necessary to counter the effects of instrumental distortion with corrections to the observed data from the transmission curve. Finally, at the highest m's and at the highest temperature, 1000° C, the indicated corrections were considered to be prohibitively large, particularly since the sensitivity of the computed γ to errors in the input data increases rapidly as strengths and widths fall. Thus the slicing method had to be abandoned in the wings of the band even though it is by far the best procedure where the lines are strong. As indicated above, these considerations will be discussed quantitatively in the section on corrections.

The strengths of the lines in the HCl 2–0 band have been measured by Benedict *et al.* (1956) using the equivalent width method. When the strengths of a few lines were measured by us as a check, values which were about 20% higher than those of Benedict *et al.* (1957) were obtained. These values agreed very well with those obtained by Kimel (1960) in this laboratory by a different method. Therefore, the strengths which were used in the present work are the smoothed Benedict *et al.* strengths increased by 20%. Those strengths were obtained by them from the experimental band strength, S_v^0, and a calculation of the individual line strengths, S_m, based on the work of Herman and Wallis (1955) as follows:

$$\frac{S_m^0}{S_v^0} = \frac{\exp[-E(J'')/kT]}{Q_J(v'',T)} \frac{\nu_m}{\nu_{v''v'}} |m| F_{v''v'}(m)$$

All the symbols used are the same as in Benedict *et al.* (1956); $F(m)$ is the correction which arises from the interaction of vibration and rotation in the Herman and Wallis (1955) approximation.

Thus, most of the measurements carried out in this work were line-width determinations. The measurements for determining γ were carried out with two cell lengths—50 cm for T = 300, 513, 1283° K and 30 cm for T = 200° K. The procedure adopted for obtaining the half width of a given line once the equivalent width had been measured and wing corrected was that of accelerated iteration described in detail by Babrov, Ameer, and Benesch (1959).

Other Methods

Two other methods of determining the line width were used for lines where the application of the two methods described above was difficult. One was the "slope method", where γ is derived from the slope, m, of the transmission curve by means of the expression

$$\gamma = \frac{SL}{\pi\epsilon + (S^2L^2m^2/4\tau^2\epsilon^2\pi)},$$

where τ is the transmission at the point where the slope is measured. The other is the "peak transmission method" where γ is obtained from the transmission at the peak of the line extrapolated to zero slit width. These methods were used in three cases only: $R(7)$ (slope), $R(8)$, and $R(9)$ at T = 200° K.

CORRECTIONS

It can be shown (Benedict *et al.* 1956), in general, that for heavily saturated lines obtained from a spectrometer which has a triangular slit function, the fractional correction to the breadth, b_ϵ, of the transmission curve can be approximated by:

$$\frac{\Delta b_\epsilon}{b_\epsilon} = \frac{d^2}{b_\epsilon^2} \frac{2\epsilon - 3}{3}.$$

This correction is seen to depend on the ratio between the slit width, d, and the transmission curve breadth, b_ϵ.

In the present work, a point by point comparison of the true and instrumentally distorted transmission curves was carried out by means of the WEIZAC computer, and the measured values of b_ϵ corrected accordingly. The maximum correction actually applied was of the order of 4% which checks well with the value obtained from the Benedict *et al.* relation.

RESULTS

The results of this investigation are given as line widths in Table I and Fig. 4 and as optical collision cross sections in Table II and Fig. 5. The experimental

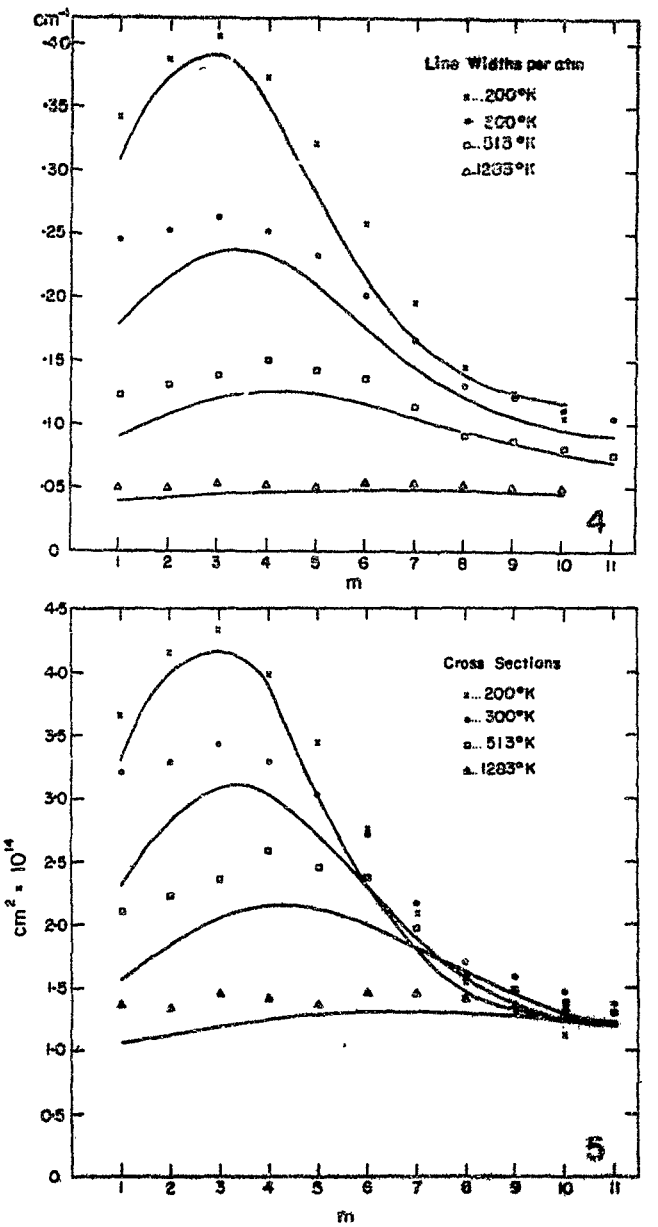

FIG. 4. The measured line widths for the *R*-branch of the HCl overtone. The values are given in units of wave numbers per atmosphere *at the temperature indicated*. The solid curves were calculated from the Anderson theory for resonant dipoles with temperature-dependent hard cores.

FIG. 5. Optical collision cross sections for the *R*-branch of the HCl overtone. The curves for the various temperatures are less disparate than those of the widths since the effect of density has been eliminated in this representation. The solid curves again give the predictions of the Anderson theory.

TABLE I

Line widths in 2–0 band of HCl

m	Experimental (cm^{-1}/atm)	Theoretical (cm^{-1}/atm)	m	Experimental (cm^{-1}/atm)	Theoretical (cm^{-1}/atm)
	$T = 200°$ K, $r_0 = 6.2$ A			$T = 513°$ K, $r_0 = 5.7$ A	
1	.342	.309	1	.123	.091
2	.389	.373	2	.130	.107
3	.403	.392	3	.138	.120
4	.373	.352	4	.151	.125
5	.322	.283	5	.143	.123
6	.259	.216	6	.137	.116
7	.196	.166	7	.115	.106
8	.145	.137	8	.092	.095
9	.123	.123	9	.087	.085
10	.105	.117	10	.081	.076
			11	.076	.070
	$T = 300°$ K, $r_0 = 6.0$ A			$T = 1283°$ K, $r_0 = 5.5$ A	
1	.245	.177	1	.050	.039
2	.251	.214	2	.049	.042
3	.262	.236	3	.054	.044
4	.251	.232	4	.052	.046
5	.231	.209	5	.051	.043
6	.207	.176	6	.054	.048
7	.165	.145	7	.053	.048
8	.130	.121	8	.052	.048
9	.121	.105	9	.050	.047
10	.112	.095	10	.049	.046
11	.104	.090			

TABLE II

Optical collision cross sections in 2–0 band of HCl

m	Experimental ($cm^2 \times 10^{14}$)	Theoretical ($cm^2 \times 10^{14}$)	m	Experimental ($cm^2 \times 10^{14}$)	Theoretical ($cm^2 \times 10^{14}$)
	$T = 200°$ K, $r_0 = 6.2$ A			$T = 513°$ K, $r_0 = 5.7$ A	
1	3.65	3.30	1	2.10	1.56
2	4.15	3.98	2	2.22	1.82
3	4.33	4.18	3	2.36	2.04
4	3.96	3.75	4	2.58	2.14
5	3.44	3.08	5	2.44	2.11
6	2.76	2.30	6	2.34	1.99
7	2.09	1.77	7	1.97	1.81
8	1.55	1.46	8	1.56	1.62
9	1.31	1.31	9	1.49	1.45
10	1.12	1.25	10	1.38	1.31
11		1.22	11	1.30	1.20
	$T = 300°$ K, $r_0 = 6.0$ A			$T = 1283°$ K, $r_0 = 5.5$ A	
1	3.20	2.31	1	1.36	1.07
2	3.28	2.80	2	1.32	1.13
3	3.42	3.09	3	1.45	1.19
4	3.28	3.08	4	1.41	1.25
5	3.02	2.73	5	1.38	1.28
6	2.71	2.31	6	1.45	1.30
7	2.16	1.90	7	1.43	1.30
8	1.70	1.56	8	1.41	1.29
9	1.58	1.37	9	1.36	1.27
10	1.46	1.24	10	1.33	1.23
11	1.36	1.18			

values are represented on the graphs as points, while the theoretical values, whose derivation is explained in the next section, are shown as solid curves.

The collision cross sections are related to the line widths by the expression

$$\gamma = (n\bar{v}/2\pi c)\sigma$$

where γ is the line width in wave numbers per atmosphere, n is the number of molecules per cc, $\bar{v}$ is the average relative molecular velocity, c is the velocity of light, and σ is the collision cross section in cm^2.

It is important to note that the values of line width are given in terms of cm^{-1} per atmosphere *at the temperature in question*. Thus the density at a pressure of one atmosphere is different for each of the various temperatures. The extent to which the variation of the line widths with temperature is attributable directly to the dependence of density on temperature may be noted by comparing Figs. 4 and 5, since the cross sections are density independent.

It is not possible to make a simple statement concerning the accuracy of the present results. Underlying all of the tabulated line widths and collision cross sections is the total band intensity value of 3.44 cm^{-2}/atm (at 300° K). The error in this figure, while probably not in excess of 5%, does not affect all of the computations uniformly. The line widths derived from equivalent widths are subject to a fractional error equal and opposite to that in the strengths. The line widths obtained from slicing (and from the other methods not involving area), however, partake of the error in strength in varying degrees and directions, the maximum fractional error amounting to perhaps twice that in the strength.

To take the 200° K widths as an example, the quality of the data changes markedly over the branch. The measurements of the first five lines are the most reliable obtained in this work, probably good to better than 5%. At the far end of the branch, at $m = 9$ or 10, the line widths are probably not reliable to better than 15%. These cases being extreme, corresponding as they do to the most and least saturated lines encountered, all of the other data should fall within these limits.

DISCUSSION

In evaluating the present results, attention must be given to the dependence of all of the computations of line width on the validity of the Lorentz line shape. In view of the experimental data, it is easy to see that in all cases the duration of collision must have been small in comparison with the time between collisions. This is a necessary condition for the validity of the Lorentz shape. On the other hand, theoretical considerations indicate that non-Lorentzian contributions may be expected to become increasingly important as one proceeds toward the far wings. As a matter of fact, experimental evidence for departures from the Lorentz line shape in the wings of strong lines has been presented by Benedict *et al.* (1956) and Smith (1961).

In deference to the foregoing considerations, detailed comparisons were made between calculated Lorentz transmission curves and the traces recorded

for the strongest lines. In no case was it possible to discern a discrepancy which could be interpreted as significant in those portions of the line from which data was taken for the width determinations. Furthermore, when the comparison was extended out as far as 10 half widths, the agreement was maintained insofar as it is possible to deduce with the available sensitivity. This does not in itself constitute an especially extensive confirmation of the Lorentz shape, but it provides an indication of the extent of the region of usefulness of the present methods.

The general pressure broadening theory of Anderson (1949) as amplified by Tsao and Curnutte (1960) is readily adaptable to the conditions of the present investigation. As indicated above, the impact approximation is valid throughout all of the ranges of pressure and temperature considered, and the resonant dipole–dipole interaction dominates all others over most of the rotational states involved. It will be seen in Figs. 4 and 5 that the application of this theory yields values of line width and collision cross section which agree well with the data in both magnitude and dependence on J.

The widths obtainable from the Anderson theory for resonant dipoles with hard cores may be expressed by

$$\gamma = \left\{L\left(\frac{273}{T}\right) \Big/ 3\hbar c\right\}\{2\mu^2 \sum f(J)\rho_{JJ} + \bar{v}(1-\sum \rho_{JJ})\pi r_0^2\},$$

where γ is the line width per atmosphere at temperature T, L is Loschmidt's number, μ is the molecular dipole moment, $f(J)$ is the J-dependent part of the generalized phase shift, ρ_{JJ} is the fractional population of the rotational state, J, $\bar{v}$ is the average relative velocity of the molecules, and πr_0^2 is a "billiard ball" cross section which is assigned to all molecular encounters which are nonresonant. The summations in this relation are over all states which are resonant with either the initial or final state of the transition leading to the absorption line in question.

Thus, following the trend of the Anderson treatment, we have so far taken r_0 as a constant and, in particular, as temperature independent. We find, however, that in order to get a reasonable fit of the calculated curves to the experimental points, we must use an r_0 which decreases as the temperature increases. The values of this hard core radius ultimately chosen to give an adequate fit were $r_0 = 6.2$, 6.0, 5.7, and 5.5 A corresponding to the temperatures 200, 300, 513, and 1283° K.

A more concise form for γ is

$$\gamma_m = a\sum f(J)\rho_{JJ} + b(1-\sum \rho_{JJ})$$

where a is proportional to $1/T$ and b is proportional to $1/\sqrt{T}$.

It can be seen, therefore, that the temperature dependence of any given line is a combination of the variation of the following quantities with temperature: (1) the density of the gas, (2) the average relative molecular velocity, (3) the population of the rotational states.

From the variation of this last quantity it can be seen that the temperature dependence of each line is also a function of m.

By considering the formula for the cross section, we eliminate the density-dependent part from the temperature variation of the line width; and we can see that that part of the cross section which depends on the resonant dipole interaction varies as the reciprocal of the velocity of the molecule. This is a feature one would expect since a molecule which moves slowly spends more time near the molecule it collides with than a fast one. In the calculated formulae for σ_m one does not see any temperature dependence in the billiard ball part of the cross section (apart from that of the $\sum_{\rho,J}$ sums). Experimentally, however, we find that in order to get a reasonable fit of the calculated curves to the experimental points we have to use a billiard ball part which decreases as temperature increases. It can be seen that the calculated curves fall somewhat below the experimental points for all temperatures. To a certain extent this is due to the choice which has been made in each case for r_0. It was felt, however, that the search for an optimum fit to the experimental data should not be allowed to obscure the fact that not all interactions have been taken into account in this treatment. For this reason the billiard ball term was purposely kept within what were considered to be judicious bounds in order to avoid a misleading compensation for the previous omissions.

If sufficiently high m lines were available experimentally, this would enable us to make an accurate determination of r_0 by fitting the theoretical curve to the experimental data, since for such high m lines ($\sim$15) the line width is for practical purposes due entirely to the billiard ball term. In such a case, the difference between the calculated and the experimental points would be due entirely to the interactions which were not taken into account. As it is, however, the presence of the band head in the R-branch makes it impossible to measure the widths of lines whose m value is larger than 10. Therefore, we cannot make an accurate determination of r_0, and have to choose a value which may be somewhat lower than the value which would be obtained were sufficiently high m lines available.

In addition to the slight general depression of the theoretical curves below the experimental points, there is the more localized separation at low J. It is here that neglect of quadrupole forces makes itself felt most strongly and where an expansion of the calculations to include higher order interactions might prove most beneficial. As a matter of fact, Herman and Benedict (1961) have shown that the theory is inherently capable of predicting widths which are in detailed agreement with the experiments. What is most urgently required for further refinements in this area is an accurate value of the HCl quadrupole moment.

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